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1. Document ID: US 6651383 B2

L6: Entry 1 of 2

File: USPT

Nov 25, 2003

US-PAT-NO: 6651383

DOCUMENT-IDENTIFIER: US 6651383 B2

TITLE: Methods of utilizing waste waters produced by water purification processing

DATE-ISSUED: November 25, 2003

INVENTOR-INFORMATION:

NAME	CITY	STATE	ZIP CODE	COUNTRY
Grott; Gerald J.	Twentynine Palms	CA	92277	

US-CL-CURRENT: 47/58.1SC

Full	Title	Citation	Front	Review	Classification	Date	Reference	Claims	KOMC	Drawn	De
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2. Document ID: US 4036749 A

L6: Entry 2 of 2

File: USPT

Jul 19, 1977

US-PAT-NO: 4036749

DOCUMENT-IDENTIFIER: US 4036749 A

TITLE: Purification of saline water

DATE-ISSUED: July 19, 1977

INVENTOR-INFORMATION:

NAME	CITY	STATE	ZIP CODE	COUNTRY
Anderson; Donald R.	Los Alamitos	CA	90720	

US-CL-CURRENT: 210/638; 203/7, 204/542, 210/259, 210/652, 210/726, 62/532

Full	Title	Citation	Front	Review	Classification	Date	Reference	Claims	KOMC	Drawn	De
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<u>L5</u>	sea water and calcium oxide and softening	19	<u>L5</u>
<u>L4</u>	sea water softeing and calcium hydroxide	0	<u>L4</u>
<u>L3</u>	sea water softeing and calcium carbonate	0	<u>L3</u>
<u>L2</u>	se water softeing and calcium carbonate	0	<u>L2</u>
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L3: Entry 3 of 10

File: USPT

Oct 8, 2002

DOCUMENT-IDENTIFIER: US 6461514 B1

TITLE: High water recovery single stage membrane process

Brief Summary Text (3):

Hardness compounds such as barium, calcium, magnesium, iron, silica, carbonate and bi-carbonate, fluoride and sulfate are commonly found in surface water supplies such as lakes and rivers as well as groundwater supplies such as water wells and aquifers and in aqueous industrial effluents and landfill leachates. Water containing hardness compounds is frequently purified by using water softeners and demineralizers in the form of "ion exchange resins, IX", chemical softeners using the cold lime or hot lime softening process, reverse osmosis (RO) membranes, nanofiltration (NF) membranes and/or distillation. Industry needs purified water containing low to very low concentrations of hardness compounds and of soluble inorganic compounds in order to supply their cooling towers, low-pressure and high pressure boilers, heat exchangers and various process uses. On the other hand, the pharmaceutical and electronics industries as well as hospitals and laboratories require high purity water that is almost completely free from inorganic compounds.

Brief Summary Text (5):

Although membrane filtration processes such as reverse osmosis (RO) and nanofiltration (NF) provide effective and economically viable methods for purifying water, these membrane processes are currently limited in the percentage of purified water produced (known as the permeate recovery or product recovery), by scale formation. Most of the soluble and scale-forming compounds are separated by the membranes and concentrated into a smaller volume, typically 20-30% of the volume of the original water stream. This membrane concentrate volume is normally too large and too costly to dispose of, except in the case of seawater desalination applications where the concentrate stream is returned to sea or where there are no regulatory limits on the concentration of inorganic compounds in the effluent. The main reason why further recovery of purified water from "conventional" RO and NF membranes is not possible is the tendency of inorganic scale such as calcium carbonate and silica to form on the surface of the membranes as the concentration of these compounds is increased beyond their saturation values. Deposition of such compounds frequently results in the loss of purified water production (also known as loss of permeate flux through the membrane) and the eventual need for costly replacement of the membranes.

Brief Summary Text (8):

U.S. Pat. No. 4,000,065 discloses the use of a combination of reverse osmosis (RO) and ultrafiltration (UF) to separate organic material from the aqueous stream. The contaminated aqueous stream is circulated from the high pressure compartment of an RO unit to the high pressure compartment of a UF unit, then to the low pressure compartment of the UF unit and then back to the high pressure compartment of the RO unit.

Brief Summary Text (10):

U.S. Pat. No. 3,799,806 discloses purification of sugar juices by repeated ultrafiltration and reverse osmosis purification steps.

Brief Summary Text (11):

U.S. Pat. No. 4,083, 779 discloses a process for treatment of anthocyanate extract by ultrafiltration and reverse osmosis treatments.

Brief Summary Text (12):

U.S. Pat. No. 4,775,477 discloses a process for extraction of cranberry presscake wherein the presscake is ground and subjected to microfiltration to remove colloidal high molecular weight compounds followed by reverse osmosis to recover a red-colored solution.

Brief Summary Text (13):

U.S. Pat. No. 5,182,023 discloses a process for removing arsenic from water wherein the water is first filtered to remove solids then passed through an ultrafilter, followed by a chemical treatment to adjust pH to a range from about 6 to 8. Thereafter, scale-inhibitors and anti-fouling materials are added before subjecting the water to reverse osmosis to provide a stream having less than about 50 ppb of arsenic.

Brief Summary Text (14):

Japanese Patent 53025-280 discloses the separation of inorganic and organic compounds from a liquid by first using a reverse osmosis membrane and then using a second reverse osmosis membrane having a more permeable membrane such as a microporous or ultrafiltration membrane. Part of the contaminated liquid obtained from the first membrane is processed through the second membrane.

Brief Summary Text (15):

U.S. Pat. No. 5,501,798 discloses a high recovery water purification process involving the use of reverse osmosis followed by chemical precipitation of hardness compounds from the RO concentrate followed by microfiltration to separate precipitated solids and recycling of the "suspended solids' free concentrate" back to the RO.

Brief Summary Text (16):

The above-referenced patents and other available literature have aimed at preventing precipitation of inorganic scale and other membrane fouling compounds as the water is treated by reverse osmosis membranes. As the concentration of scale and other inorganic and organic fouling compounds build up on the surface of the RO membranes, the purified water permeation rate deteriorates with eventual irreversible loss of productivity and need for costly membrane replacement. Prior art teaches acidification (i.e. pH reduction) as a means of reducing the potential of calcium carbonate scale formation. Prior art also teaches the addition of scale inhibitors such as polyacrylic acids and sequestering agents such as ethylene diamine tetracetic acid (EDTA) and sodium hexametaphosphate (SHMP) in order to reduce the scale formation potential due to barium sulfate, calcium fluoride, calcium and magnesium carbonate and sulfate and silica. However, these scale inhibitor compounds are not sufficiently efficient to allow very high water recoveries and concentration factors to be achieved. Maximum recoveries in the presence of scale inhibitors may be in the range 70%-75%, based on the treatment of hard "well-water". The above-referenced patents also teach the separation of suspended solids existing originally in natural water sources and industrial effluents or the separation of chemically-precipitated compounds using ultrafiltration or microfiltration before reverse osmosis treatment. While removal of suspended solids by membrane filtration will prevent fouling of the RO membranes, it does not prevent concentration and eventual deposition of the initially soluble scale compounds, as the recovery of purified water is increased using RO. U.S. Pat. No. 5,501,798 teaches a high recovery process involving the use of a single stage reverse osmosis system, chemical precipitation and microfiltration (MF) and recycling of MF permeate to the RO membrane system to maximize the recovery of purified water. However, high water recovery from the process of U.S. Pat. No. 5,501,798 is limited by the maximum RO membrane system operating pressure of 1,000 psig. The process of U.S. Pat. No. 5,501,798 also has

the inherent disadvantage of high capital and operating cost associated with the chemical precipitation step and the suspended solids separation step. The suspended solids in the supernatant from the precipitation step are separated by microfiltration membranes or other separation means and the softened MF membrane permeate or filtrate is recycled to the RO membranes in order to minimize the scale formation potential on these membrane.

Drawing Description Text (2):

In the drawings which illustrate embodiments of the invention, FIG. 1 (FIG. 1) is a schematic representation of the proposed economical high recovery single stage membrane process for the purification of small flowrates of raw water 1 containing low to moderate Total Dissolved Solids (TDS) with moderate to high hardness, where a good quality of treated water 16 is required with a minimum reject volume 13.

FIG. 1 shows a raw water pretreatment step 2 intended to remove suspended matter by using suitable pretreatment means including coagulation, flocculation, clarification, multi-media filtration, ultrafiltration or microfiltration.

Pretreatment is followed by a single stage reverse osmosis (RO) or nanofiltration (NF) membrane system 7, where the pre-treated water is pressurized and introduced into the high pressure side of said RO or NF membranes and a very large portion of the water is purified, providing a purified water (i.e. membrane permeate) stream 16. In order to prevent scale formation on the surface of the membranes, an efficient ion exchange (IX) water softening resin 17 is used to treat the RO or NF membrane concentrate stream 12, thereby removing the water hardness and providing a softened membrane concentrate stream 18. The said softened membrane concentrate stream 18 is recycled and blended with the pre-treated hardness-containing raw water (i.e. stream 3) before introducing the blended stream 6 to the membrane system 7.

Detailed Description Text (2):

When using a semi-permeable membrane such as reverse osmosis (RO) or nanofiltration (NF) to purify water, the soluble inorganic ions such as sodium, potassium, calcium, magnesium, iron, chloride, fluoride, carbonate, bicarbonate, sulfate and silica are separated by the membrane while the water is allowed to permeate or pass through the membrane. While RO membranes separate all inorganic (and indeed organic) species, NF membranes are somewhat "looser" than RO membranes and have selectivity for separation of divalent and other multivalent ions such as carbonate, phosphate, silicate, sulfate, aluminum, barium, calcium, magnesium, strontium, chromium, copper, lead, nickel, silver, tin, titanium, vanadium, zinc and other multivalent cations of the periodic table, while allowing monovalent ions such as sodium, potassium, cesium, chloride, fluoride, nitrate and other monovalent ions to permeate through the membrane. NF membranes are therefore typically used to remove "hardness" and other sparingly soluble compounds from the water (i.e. calcium, magnesium, silica, etc.). Typically, the water solubility of these hardness ions, when combined with certain monovalent, divalent or multivalent anions such as fluoride, carbonate, hydroxide, phosphate and sulfate (e.g. calcium fluoride, calcium or magnesium carbonate, calcium or magnesium silicate and calcium sulfate) is rather low when compared to compounds of monovalent cations such as sodium chloride, sodium carbonate or sodium sulfate. These compounds of multivalent cations are therefore termed "sparingly soluble compounds" and such term will be used extensively in the present invention.

Detailed Description Text (6):

In the present invention, the limitations on the permeate recovery from a semi-permeable membrane (e.g. reverse osmosis, RO or nanofiltration, NF) which were experienced in prior art are completely eliminated while simultaneously reducing the overall cost and rendering the single stage high water recovery process economically viable. This is achieved in the case of small flowrates and moderate to high water hardness by employing a single stage membrane process in which the membrane concentrate is recycled directly to the influent, high-pressure side of the membrane after a simple and cost-effective hardness removal treatment step. In

contrast to the costly and complex chemical precipitation and microfiltration treatment of the membrane concentrate in the prior art (viz. U.S. Pat. No. 5,501,798), the hardness removal step in the present invention comprises a simple and yet effective ion exchange softening resin (viz. IX water softener). By continuously removing the hardness cations and other heavy metals (i.e. calcium, magnesium, barium, iron, etc.) from the membrane concentrate and recycling the softened concentrate to the inlet side of the membrane for further purification, high overall permeate recoveries can be achieved without scale formation.

Detailed Description Text (8):

Thus, for example, FIG. 1 provides a schematic illustrating the process of the invention which treats small water flowrates of 5-50 U.S. gpm, containing inorganic contaminants with low to moderate TDS concentration of 100-1000 mg/liter and preferably 200-400 mg/liter and moderate to high hardness in the range 100-1000 mg/liter as CaCO₃ and normally 100-200 mg/liter CaCO₃. In accordance with this invention, it is possible to achieve permeate recoveries in the range 67%-99.9% without the deposition of inorganic scale on the surface of the membrane. As shown in FIG. 1, the Raw Water or Influent Water 1 is introduced into a suitable Pretreatment Means 2 consisting of a clarifier or gravity settler with or without the use chemical coagulants and/or flocculants or alternatively by using an air flotation device, to be followed by a single media or multi-media filtration device followed by a cartridge filter in the 5-10 micron particle separation range. Alternatively, the Influent Water 1 is pretreated by a suitable nonfouling ultrafiltration or microfiltration membrane such as but not limited to tubular or hollow fiber membranes or any suitable combination of the above pretreatment means which will efficiently separate oil and grease, colloidal iron and other suspended solids and prevent premature fouling and "surface blinding" of the membranes 7 downstream.

Detailed Description Text (10):

The pretreated and preconditioned stream 6 in the embodiment of FIG. 1 is introduced into the high pressure side of the single stage membrane system 7 consisting of a suitable semipermeable membrane selected from a group of spirally wound, hollow fiber, tubular, plate and frame and disc-type nanofiltration (NF) and reverse osmosis (RO) membranes. Purified water permeate 16 containing a much lower concentration of TDS is recovered on the low pressure side of the semi-permeable membranes and the membrane concentrate 12 is removed from the high pressure side of the membranes and subjected to further treatment in order to increase the purified water recovery. The membrane system's operating pressure will be determined by the Influent Water TDS concentration and the desired permeate recovery since these parameters will determine the osmotic pressure exerted by the solution. In general, the higher the initial TDS and/or the higher the desired permeate recovery, the higher the operating pressure. As an example, for an influent TDS of 200 mg/L, an operating pressure in the range 400-500 psig will be required to achieve a permeate recovery of 98-99%, based on the Influent Water volume 1. It will be noted, however, that as the permeate recovery is increased, the purified (i.e. permeate) water quality deteriorates.

Detailed Description Text (23):

Yet another embodiment of this invention is represented schematically in FIG. 3 which illustrates another economical high recovery single stage membrane process for the purification of small volumes of water containing relatively low TDS and low to moderate hardness. In addition to the need for a minimum volume of reject stream 13, it is also desired to provide a membrane permeate with very high purity, as required by the pharmaceutical industry. This embodiment of the invention, as represented in FIG. 3, provides an improvement over the embodiment illustrated in FIG. 2 by introducing the membrane permeate 16 into a second pass semi-permeable membrane purification step 27. This second pass membrane step 27 will preferably consist of reverse osmosis membranes or "tight" nanofiltration membranes. In this manner, this embodiment of the invention will provide a purified water stream 29

with an electrical resistivity >2 mega ohms (i.e. electrical conductivity <0.5 .mu.S/cm) at a high overall system recovery in the range 90%-99%, depending on the influent water TDS. In order to minimize the reject stream volume 13, the second pass membrane concentrate 28, which contains relatively low TDS and very low hardness, is recycled to the high pressure side of the first pass membrane system 7 where it is purified further resulting in increased overall process permeate recovery. As before, the TDS and osmotic pressure of the first pass membrane concentrate stream 12 are controlled by removing and disposing of a small volume of reject stream 13 under flow control.

Current US Original Classification (1):
210/652

CLAIMS:

1. An improved high recovery single stage single pass membrane process for the economical operation of semi-permeable reverse osmosis (RO) membranes which are used to purify low flowrates of water containing low concentrations of soluble and sparingly soluble inorganic compounds and achieve high recoveries of purified water in the range 95%-99.9% of the Influent Water without precipitation of sparingly soluble inorganic scale compounds on the surface of the membrane, comprising: (a) pretreating the Influent Water using a suitable pretreatment means to separate all suspended solids, oil and grease and iron and produce pretreated water; (b) blending said pretreated water containing soluble and sparingly soluble inorganic compounds with a large, softened, membrane concentrate recycle stream containing a high concentration of Total Dissolved Solids (TDS) to produce a blended feed stream; (c) pre-conditioning said blended feed stream by adding acid and antiscalant in order to produce a preconditioned blended feed stream having a low scale forming tendency; (d) introducing said preconditioned blended feed stream into the high pressure side of the single stage single pass RO membranes; (e) pressurizing said preconditioned blended feed stream on said high pressure side of said single stage single pass RO membranes to produce purified water permeate on the low pressure side of said single stage single pass RO membranes substantially free of said inorganic compounds; (f) removing a membrane concentrate stream containing pre-concentrated soluble and sparingly soluble inorganic compounds from said high pressure side of said single stage single pass RO membranes without precipitation of said pre-concentrated sparingly soluble inorganic compounds on said single stage single pass RO membranes; (g) recovering said purified water permeate on said low pressure side of said single stage single pass RO membranes at a rate in the range 95%-99% of the rate of introducing said Influent Water containing said soluble and sparingly soluble inorganic compounds to said high pressure side of said single stage single pass RO membranes; (h) introducing said RO membrane concentrate stream into an ion exchange water softer resin which separates and retains the hardness due to said sparingly soluble inorganic compounds to provide a softened, high TDS RO membrane concentrate stream; (i) recycling said softened, high TDS RO membrane concentrate stream at a flow of 40%-60% of the flow rate of the Influent Water and blending it with said pretreated water to produce said blended feed stream which is preconditioned and introduced into said high pressure side of said single stage single pass RO membranes; (j) removing a small RO membrane reject stream from said RO membrane concentrate stream at a rate in the range 0.1% to 5% of the rate of introducing said Influent Water to said high recovery single stage single pass membrane process in order to control the concentration of said soluble inorganic compounds and hence the osmotic pressure; (k) disposing of said small RO membrane reject stream to drain or via other suitable waste disposal means.

15. An improved high recovery single stage double pass membrane process for the economical operation of semi-permeable reverse, osmosis (RO) membranes which are used to purify low flowrates of water containing low concentrations of soluble and sparingly soluble inorganic compounds and achieve high recoveries of very high purity water in the range 67%-99.9% of the Influent Water without precipitation of

sparingly soluble inorganic scale compounds on the surface of the membrane, comprising: (a) pretreating the Influent Water using a suitable pretreatment means to separate all suspended solids, oil and grease and iron and produce pretreated water; (b) blending said pretreated water, containing soluble and sparingly soluble inorganic compounds, with a large, softened, membrane concentrate recycle stream containing a high concentration of Total Dissolved Solids (TDS), with a recycled purified water permeate from the low pressure side of the first pass membranes of said single stage membrane processed and with a relatively low TDS second pass RO membrane concentrate to produce a blended feed stream; (c) preconditioning said blended feed stream by adding acid and antisiscalant in order to produce a preconditioned blended feed stream having a low scale forming tendency; (d) introducing said preconditioned blended feed stream into the high pressure side of the first pass membranes of said single stage double pass membrane process; (e) pressurizing said preconditioned blended feed stream on said high pressure side of said first pass membranes of said single stage double pass membrane process to a pressure in the range 100-3000 lb/square inch (psig), to produce purified water permeate on the low pressure side of said first pass membranes substantially free of said inorganic compounds; (f) removing an RO membrane concentrate stream containing pre-concentrated soluble and sparingly soluble inorganic compounds from said high pressure side of said first pass membranes of said single stage double pass membrane process without precipitation of said pre-concentrated sparingly soluble inorganic compounds on said first pass membranes; (g) recovering said purified water permeate on said low pressure side of said first pass membranes at a rate in the range 67%-99.9% of the rate of introducing said Influent Water containing said soluble and sparingly soluble inorganic compounds to said high pressure side of said first pass membranes of said single stage double pass membrane process; (h) introducing said RO membrane concentrate stream into an ion exchange water softening resin selected from a group consisting of chelating resins, weak acid cation exchange resins, strong acid cation exchange resins in their sodium form and a combination of fixed bed and continuous cation exchange systems which separate and retain the hardness due to said sparingly soluble inorganic compounds to provide a softened, high TDS RO membrane concentrate stream; (i) recycling said softened, high TDS RO membrane concentrate stream and blending it with said pretreated water, said recycled purified water permeate and said relatively low TDS second pass RO membrane concentrate to produce said blended feed stream which is preconditioned and introduced into said high pressure side of said first pass membranes of said single stage double pass membrane process; (j) removing a small RO membrane reject stream from said RO membrane concentrate stream at a rate in the range 0.1% to 33% of the rate of introducing said Influent Water to said high recovery single stage double pass membrane process in order to control the concentration of said soluble inorganic compound and hence the osmotic pressure; (k) disposing of said small RO membrane reject stream to drain or via other suitable waste disposal means; (l) recycling a fraction of said purified water permeate from said low pressure side of said first pass membranes of said single stage double pass membrane process to said high pressure side of said first pass membranes at a rate in the range 10%-100% of the rate of introducing said Influent Water to said high recovery single stage double pass membrane process, in order to produce high purity water on the low pressure side of said first pass membranes; (m) adjusting the pH of said high purity water to the neutral range 6-8 to produce pH-adjusted high purity water; (n) introducing said pH-adjusted high purity water into the high pressure side of second pass RO membranes of said single stage double pass membrane process; (o) pressurizing said pH-adjusted high purity water on the high pressure side of said second pass RO membranes to provide a very high purity water permeate on the low pressure side and to provide a relatively low TDS second pass RO membrane concentrate on the high pressure side of said second pass RO membranes; (p) removing said relatively low TDS second pass RO membrane concentrate from the high pressure side of said second pass RO membranes at a rate sufficiently high to ensure very high purity of said very high purity water permeate; (q) recovering said very high purity water permeate having an electrical resistivity >2 mega ohms from said low pressure side of said second pass RO

membranes at a rate in the range 50%-90% of the rate of introducing said pH-adjusted high purity water into said high pressure side of said second pass RO membranes; (r) recycling said relatively low TDS second pass RO membrane concentrate from said high pressure side of said second pass RO membranes to said high pressure side of said first pass membranes of said single stage double pass membrane process to achieve further purification and further increase the recovery of said very high purity water permeate.

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approximately 25 percent of the water processed to waste facilities, thereby inhibiting the efficiency of the process and presenting a disposal problem of considerable magnitude.

Brief Summary Text (9):

Various techniques have been suggested for the pretreatment of saline water to improve the efficiency of their subsequent desalination treatment. One method, described in U.S. Pat. No. 3,262,865, discloses that the deposition of scale in a water distillation process can be inhibited by acidifying the raw water with sulfuric acid. Another pretreatment method, disclosed in U.S. Pat. No. 3,639,231, comprises the ion exchange of the raw water prior to its desalination treatment with reverse osmosis. A number of processes have also been developed for a chemical water softening of waters which contain hardness ions such as calcium and magnesium. Typically, these processes comprise the addition of calcium hydroxide alone or in combination with sodium carbonate to reduce the solubility of the dissolved calcium carbonate in the water. Typical of such treatments is that disclosed in U.S. Pat. No. Pat. 3,740,330. These treatments, however, are not generally applicable to desalination treatments because they do not sufficiently reduce the concentration of scale-forming dissolved salts in the processed water.

Brief Summary Text (11):

This invention comprises a method for the pretreatment of water and is useful in combination with a subsequent processing involving concentration of the water such as a desalination process, e.g., distillation, reverse osmosis, vapor compression, electrodialysis, freezing, ion exchange, etc., or use of the water in evaporative cooling or as boiler feedwater. The pretreatment method as applied to any of these processes results in a substantial decrease in the scale-depositing impurities of the water prior to the salt concentrating steps of the aforementioned water processes. The method also utilizes precipitants obtained in subsequent steps of the process and thereby is substantially self-sufficient in reagents.

Detailed Description Text (2):

Referring now to FIG. 1, there is illustrated a flow diagram of a desalination process utilizing the pretreatment method of this invention. In this application, the raw saline water enters the process at line 10. This water can be agricultural drain water, brackish water and the like, which generally has a dissolved salts content no greater than about 10,000 ppm. Waters which have greater salt contents and, in particular, sea water, which also has a disproportionately high magnesium content, can not be readily treated by this process because of high solubility activities and tendency of magnesium to complex calcium which greatly increase the solubility of calcium. It is also desirable that the sulfate content of the water be less than about 2500 ppm and, most preferably, less than about 1500 ppm to avoid excessive precipitation of calcium sulfate in the treated reject brine of the process. The inlet water can be screened and filtered, if necessary, to separate floating debris and suspended solids such as grit, sand and the like.

Detailed Description Text (10):

The separation of the calcium carbonate is completed in step 18 where the treated water is processed using conventional equipment, such as settling vessels, precipitators, flotation devices and the like to separate the calcium carbonate flock from the water. Useful equipment for this treatment can be the conventional equipment in chemical water softening such as a sludge blanket precipitator or settler where the calcium carbonate sludge is accumulated and freshly treated water is passed upwardly through the precipitated material.

Detailed Description Text (14):

The formation of a brine in step 34 can be accomplished by any of a plurality of processes. A preferred process is reverse osmosis in which the water is pressured to about 200-1,000 p.s.i.g. and passed across a reverse osmosis membrane, typically formed of cellulose diacetate or polyamides, e.g., Nylon and related materials.

These membranes are permeable to water but impermeable to dissolved salts. Under the applied pressure, osmosis occurs in the reverse direction, i.e., from the concentration saline water to a purified water on the opposite side of the membrane. Typically, treated water substantially reduced in salt content is produced through line 36 at a rate from 5 to about 20 gallons per square foot of membrane per day with power requirements of from 6 to 11 kilowatt hours per 1,000 gallons of deionized water. The membranes are supported against the applied pressure of the saline water by use of a plurality of configurations such as tubular liners, tubular wraps, spiral wound systems and hollow, fine fibers. Examples of these are spiral wound cellulose acetate membranes marketed by Gulf General Atomic and the hollow fibers of polyamides manufactured by E. I. DuPont de Nemours, Wilmington, Delaware.

Detailed Description Text (20):

Referring again to FIG. 1, the rejected brine from the process, regardless of the nature of the desalinization process conducted in step 34, is removed through line 38 and is subsequently treated in accordance with the invention. This brine is passed into mixing zone 40 where it is contacted with a supply of calcium hydroxide through line 42. The calcium hydroxide used in the process is, preferably, obtained from the calcium carbonate sludge passing through line 28. The produced calcium carbonate is introduced through line 28 into a furnace or kiln in a calcination step 42 where it is heated to a high temperature, above its decomposition temperature of 825.degree. C, preferably, between about 850.degree. and 1200.degree. C. sufficient to decompose the calcium carbonate and release carbon dioxide through line 46. The resultant, powdered calcium oxide is removed from the calcination step 44 through line 48 and passed into admixture with sufficient water to slake the calcium oxide in step 47 and produce calcium hydroxide which is supplied to the mixing step 40 through line 42.

Detailed Description Text (26):

Carbon dioxide, which can be recovered from the calcination of the calcium carbonate and/or the combustion gases formed by burning of fuel in step 44, can be passed through line 60 into contact with the treated brine from the magnesium hydroxide separation zone 50 to lower its pH value to acceptable, near-neutral values of from 7 to about 8. The neutralization of this brine results in the precipitation of a substantial quantity of calcium carbonate that is removed through line 65. All or a portion of the separated calcium carbonate can be disposed as a waste product or recovered as a useful by-product of the process through line 67. Alternatively, the calcium carbonate can be passed through line 69 to the calcination step 44 to obtain calcium oxide therefrom which could be a useful product, e.g., for Portland cement manufacture and the like, and removed through line 71. Alternatively, all or most of the calcium oxide produced in the step 44 could be passed to the slaking step 47 and converted into calcium hydroxide with the excess calcium being removed from the process through line 73 as calcium hydroxide, should the latter be a useful or desirable by-product of the process.

Detailed Description Text (31):

Sufficient sulfuric acid is added to the treated water to reduce its pH level to 6.0 and the water is processed through a reverse osmosis treatment to recover a purified and substantially deionized water therefrom which comprises approximately 90 percent of the raw saline water to the treatment. The salt rejection efficiency of the reverse osmosis treatment is about 94 percent. The rejected brine from the reverse osmosis treatment comprises 10 percent of the saline water to the treatment and this brine has the following composition:

Detailed Description Text (34):

The treated brine can, thereafter, be carbonated by contacting carbon dioxide therewith to reduce its pH to an acceptable, near-neutral level, e.g., from 7 to about 8. The addition of the carbon dioxide to the brine results in additional precipitation of calcium carbonate which is permitted to settle and is removed from

the process in an amount comprising 14 milliequivalents per liter of brine. The calcium carbonate recovered in this step can be combined with that separated from the raw saline water in the initial pretreatment and calcined at a temperature of about 850.degree. C. to prepare calcium oxide therefrom. This calcium oxide can be slaked to produce all of the requirements of the calcium hydroxide utilized in the process.

Detailed Description Text (36):

This example illustrates that the precipitation of magnesium hydroxide is sufficiently rapid to permit its separation from a calcium sulfate containing brine. In this experiment, a brine was prepared having a composition of dissolved salts as would be obtained from a reverse osmosis process practiced on typical agricultural drain water in which 15 percent of the raw water is rejected as residual brine. This brine was prepared by dissolving salts in distilled water to obtain a brine of the composition indicated in the following table:

Detailed Description Text (46):

The following will illustrate the application of the process to a treatment plant capable of processing 110 million gallons of saline water per day. The saline water can be initially treated with an oxidant such as an alkali metal permanganate to oxidize dissolved ferrous ions to the ferric ions, decreasing their solubility and precipitating ferric salts from the saline water. The water is then passed into a mixing zone and is contacted therein with magnesium hydroxide supplied thereto at a rate of 75.2 tons per day, resulting in the formation of a flocculant precipitate which is separated in the succeeding flocculation and settling stages as insoluble calcium carbonate in a quantity comprising 251 tons per day. The water is acidified by the addition of sulfuric acid to reduce its pH to an acceptable treatment level, typically to a value of 6.0. The treated water is thereafter passed through a reverse osmosis process to produce deionized water at a rate of 10 million gallons per day and a concentrated brine at the rate of 10 million gallons per day.

Detailed Description Text (47):

The calcium carbonate separated from the pretreatment step and recovered in subsequent brine processing is passed to a kiln and is burnt therein at a temperature of about 925.degree. C. to decompose the carbonate and produce 223 tons per day of calcium oxide which is slaked by the addition of water to produce 334 tons per day of calcium hydroxide. The calcium hydroxide is added to the brine separated from the reverse osmosis treatment resulting in the precipitation of 187 tons per day of magnesium hydroxide which is separated from the brine. Half of the magnesium hydroxide so separated, 93.5 tons per day, is used as the magnesium precipitant in the pretreatment of the saline water and the balance of the magnesium hydroxide is passed into a carbonation zone where it is converted to magnesium bicarbonate by contacting with carbon dioxide while suspended in an aqueous medium.

CLAIMS:

1. A method for selectively removing calcium salts from raw water containing dissolved salts, including calcium bicarbonate, in a total amount no greater than about 10,000 parts per million, and for purifying the water wherein said dissolved salts in said raw water are concentrated in a residual portion during said purification thereof to a content approaching their solubility limits at the purification processing conditions, which comprises the following sequential steps for reducing the volume of said residual portion:

a. adding magnesium hydroxide precipitant to the raw water in an amount sufficient to precipitate calcium carbonate settling said precipitate, and recovering a treated water having a substantially reduced dissolved calcium content that said raw water and passing said treated water to said processing;

b. processing said treated water to separate a purified water from a residual water enriched with salts by reverse osmosis, distillation, electrodialysis or freezing;

c. adding calcium hydroxide to at least a portion of the residual water from said processing in an amount sufficient to precipitate soluble magnesium values in said waste brine as insoluble magnesium hydroxide; and

d. separating magnesium as magnesium hydroxide from said waste brine and returning the separated magnesium hydroxide as substantially the entirety of the precipitant to step (a).

6. The method of claim 1 wherein said processing comprises the forcing of said treated water through a reverse osmosis membrane to obtain a purified effluent and to concentrate dissolved salts contained in said treated water in said residual portion.

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L6: Entry 2 of 2

File: USPT

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TITLE: Purification of saline water

Abstract Text (1):

There is disclosed a treatment of water that greatly reduces the scaling tendency of the water during its subsequent use or processing. The treatment comprises precipitation and separation of the calcium values of the water as calcium carbonate by the addition of magnesium hydroxide precipitant thereto, with, as needed, a carbonate source, e.g., carbon dioxide. During subsequent use or processing, salts dissolved in the water are concentrated in a residual portion thereof and the residual portion is processed by the addition of calcium hydroxide to precipitate the dissolved magnesium values from the residual portion and supply the magnesium hydroxide that is employed as the precipitant in the treatment of the raw water. The treatment can be applied to any of a variety of water treating processes such as reverse osmosis, distillation, electrodialysis, freezing, vapor compression, ion exchange, evaporative cooling and/or boiler feed water treatment. All of these processes are limited in efficiency and equipment design by the concentration of calcium salts in the residual water which rapidly approach their solubility limits as the water is concentrated, thereby inhibiting further concentration or forming of scale on the separation equipment during the salt concentration steps of the treating process. This invention greatly increases the operating efficiency of salt concentration processes by reducing the tendency of the water to form scale during its processing.

Brief Summary Text (6):

Various methods have been proposed for desalinization of saline water such as agricultural drain waters or industrial waste waters. Such treatments include distillation, reverse osmosis, electrodialysis, freezing, ion exchange and vapor compression which all effect separation of a purified water of greatly reduced salt content from a brine that is concentrated in the impurities present in the saline water. When the saline water is purified, the impurities in the brine rapidly reach their solubility limits at the treatment conditions and the brine becomes super-saturated. The super-saturated brine presents a number of difficulties in the purification treatment; it can cause the formation of scale on equipment such as the heating surfaces used in distillation, the heat exchange surfaces used for cooling of the water in freezing purifications, or the equipment surfaces used in vapor compression. Additionally, the efficiency of membrane processes such as reverse osmosis or electrodialysis is greatly reduced by scaling the membrane and precipitation formation in the brine channels of the equipment. In ion exchange water treatments, sulfuric acid is commonly used to regenerate spent cationic resins and the presence of calcium in the spent resin can result in the precipitation of calcium sulfate in the resin during its regeneration.

Brief Summary Text (8):

In reverse osmosis units, agricultural drain water can only be concentrated about three-fold before the precipitates of calcium sulfate greatly scale the membrane and plug the equipment brine channels in the reverse osmosis unit. As a result, most reverse osmosis processes on saline waters require the discharging of